

GLASS IN CULTURAL HERITAGE – AN INTRODUCTION

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Abstract

A brief description of different types of silicate glasses is made and the origin of colour in glasses is discussed. The principles of corrosion in glass, illustrated with a few examples, will be explained. Applications of several techniques in the chemical characterization of glasses will be shown, namely X-ray Fluorescence Spectrometry (XRF), Scanning Electron Microscopy (SEM), Optical Absorption Spectroscopy and Laser Ablation Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (LA-FTICR/MS), and Particle Induced X-ray Emission (PIXE).

Keyword: glass; cultural heritage; glass analysis; glass corrosion; colour in glass

Introduction

“A glass can be defined as “an amorphous solid completely lacking in long range, periodic atomic structure and exhibiting a region of glass transformation behaviour “

James Shelby [1]

Figures 1 and 2 shows the non repetitive order at long range in silica glass and the transition temperature, respectively.

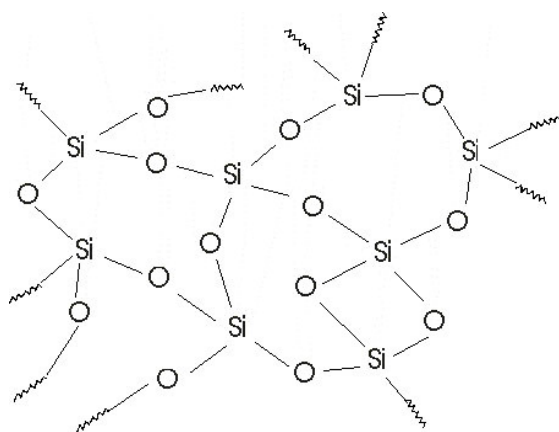


Fig. 1. 2D representation of a silica glass.

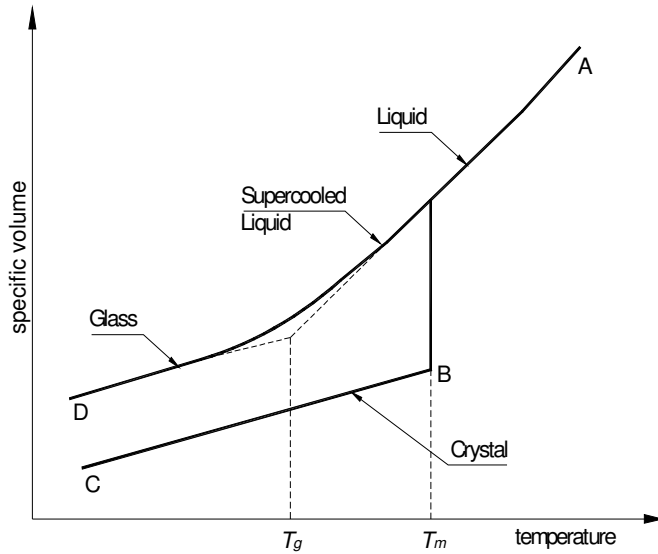


Fig. 2. Variation of the specific volume with temperature during the solidification of crystalline and vitreous material. T_g is the glass transition temperature of the amorphous material. T_m is the melting temperature of the crystalline material.

The glass transition is transition in which a supercooled melt yields, on cooling, a glassy structure. Below the glass-transition temperature the physical properties vary in a manner similar to those of the crystalline phase. The transition is not as dramatic as the phase change that takes you from liquid to crystalline solids. Batch materials to make glass can be grouped in network formers (SiO_2 , B_2O_3 , P_2O_5 , GeO_2 , As_2O_3 , Sb_2O_3), fluxes/network modifiers (Na_2CO_3 , Na_2SO_4 , K_2CO_3 , Li_2CO_3 , PbO), network stabilizers (CaCO_3 , Al_2O_3 , PbO), colourants and fining agents. PbO can be used as a flux or, if substituting the silicon in the network, as network former. In Table 1 examples of compositions of different types of glass are shown.

Table 1. Compositions of different types of glass.

	Bottle glass ¹	Goblet glass ¹	Window glass ¹	Lead glass ¹	Borosilicate glass ²
SiO_2	53.55	75.9	69.75	56.0	73 - 82
Na_2O		17.5	15.22	2.6	3 - 10
K_2O	5.48			8.9	0.4 - 1
CaO	29.22	3.8	13.31		0 - 1
MgO					
Al_2O_3	6.01	2.8	1.82		2 - 3
PbO				32.5	0 - 10
B_2O_3					5 - 20
Fe_2O_3	5.74				

1- from ref. [2] ; 2 - from ref. [3]

Glazes used for ceramics can be considered as thin layers of glass. They are made by firing a mixture of batch materials, being the composition defined to obtain a desired melting temperature. In Table 2 are indicated the oxides which can be part of a glaze.

Table 2. Oxides used in glazes.

RO, R ₂ O	R ₂ O ₃	RO ₂
BaO	Al ₂ O ₃	SiO ₂
CaO	B ₂ O ₃	SnO ₂
PbO		TiO ₂
Li ₂ O		ZrO ₂
MgO		
K ₂ O		
Na ₂ O		
ZnO		

Colour in glass

The colour in glass can be due to *d-d* electronic transitions, charge transfer between cations and anions (e.g. $\text{Fe}^{3+} \rightarrow \text{O}^{2-}$), interaction of the light with small particles (Cu, Ag, Au and cadmium sulfoselenide), interaction of the light with small crystals formed during the cooling of glass due to devitrification (light diffusion – opaline glass) and optical interference in thin layers.

The *d* transition elements have *d* orbitals incompletely filled and the *d* electronic levels are identical in energy for free ions. In a glass the metal ions are surrounded mainly by oxygen ions and the interaction of the electric field causes a small splitting of the energy levels. The value of this splitting depends on the field strength caused by the surrounding ions, the coordination number and the geometric arrangement around the central ions. Fig. 3 exemplifies the ligand field splitting in two complexes with different symmetry. The tetrahedral and octahedral coordination around Co^{2+} ions in glass gives absorption bands around 530 nm and 680 nm respectively, being the glasses formed rose and blue, respectively. An analogy with the complexes $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{CoCl}_4]^{2-}$ in aqueous media with similar colours can be made. An interesting example of the influence of the ligand field strength in the colour is given by Shelby [1] for a borosilicate glass with Co^{2+} which is dark blue purple. Substituting partially the oxygen anion by Cl^- , Br^- or I^- , light blue green, green and red-brown colours are respectively observed.

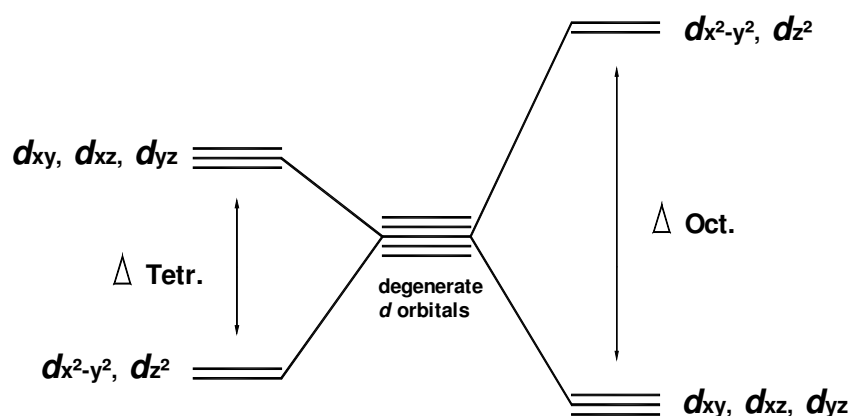


Fig.3. Ligand field splitting in tetrahedral and octahedral complexes.

When preparing a coloured glass using a *d* transition element it is important to define an adequate composition which can affect the ligand field. The oxidation state of the cation can be controlled with a reducing or oxidizing atmosphere in the furnace.

The *d* transition elements impart to the glass a varied palette of colours. A few examples are given in Table 3.

Table 3. *d* transition elements and colour in glass.

Ion	Coordination	Colour
Cr ³⁺	Octahedral	green
Cr ⁶⁺	Tetrahedral	yellow
Fe ²⁺	Tetrahedral	blue
Co ²⁺	Tetrahedral	blue
Co ²⁺	Octahedral	rose-purple
Cu ²⁺	Octahedral	blue

When characterizing a glass by optical absorption spectroscopy it is important to obtain the spectrum values for the UV, Visible and Near Infrared range. Fig. 4 shows the absorption zones and the respective responsible phenomenon. Intense bands with a maximum in the UV range can give origin to colour as the band spreads to the visible range.

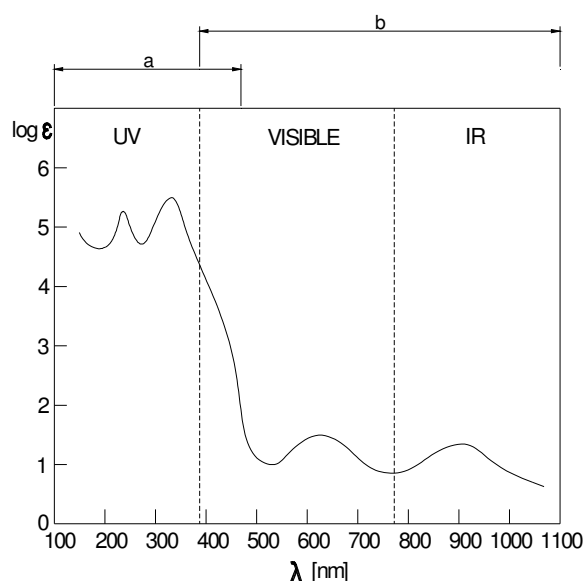


Fig. 4. a) Absorption bands of the ligand or due to electronic transitions between the ligands and the central cation; b) absorption bands due to transitions of *d* electrons between different energy levels.

The colour can also be due to interaction of the electromagnetic radiation with small particles: Ag (silver yellow), Cu or Au (ruby copper or ruby gold), cadmium sulfoselenides (red glass).

When $\text{CdSe}_x\text{Te}_{1-x}$ particles are introduced into glass batches, the pigment currently used for making red glasses, the glasses formed contain semiconductor particles. The absorption spectra depend on the concentration and size of the nanoparticles. Photons with energies greater than the band gap of the semiconductor undergo absorption and consequently the optical absorption spectra have a sharp transmission cut-off. The bands gaps of CdSe and CdS are 1.67 eV (724 nm) and 2.53 eV (490 nm) respectively. The colour can be controlled by changing the ratio of the two compounds, varying from yellow to dark red. A spectrum of a glass goblet containing sulfoselenide is shown in Fig. 5.

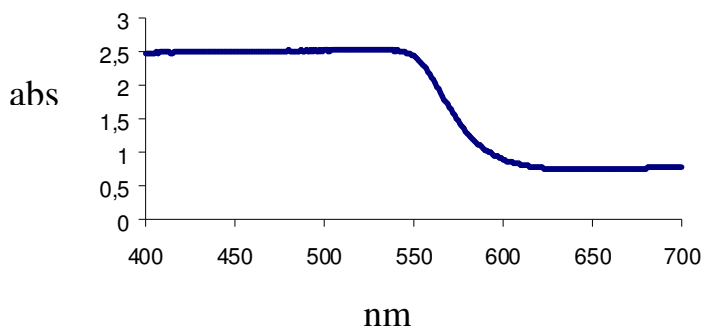


Fig. 5. Optical absorption spectrum of the red stem of a goblet from Fábrica-Escola Irmãos Stephen, Glass Museum of Marinha Grande.

In the gold and copper ruby glasses as in the yellow silver staining in stained glass, the colour is due to the interaction of the electromagnetic radiation in the visible range with metal nanoparticles, originating absorption bands around 530 nm for gold, 565 nm for copper and 410 nm for silver. These bands can be considered as plasma resonance bands as the free electrons in the particles behave as a bounded plasma [1,4].

One of the first written documents where there is a recipe for making ruby glass was published by Antonio Neri in his famous book “L’Arte Vetraria” [5]. Later, a report written by Kunckel describes the manufacture of gold ruby glass [6]. Since then, gold ruby glass was produced in several places in Europe. This production seems to have started in the 17th century when “Purple of Cassius” was added to the glass batch compositions [7]. Purple of Cassius is a colloidal suspension of gold obtained by reducing a gold (III) chloride aqueous solution with stannous chloride. Fig. 6 shows a goblet made of ruby gold glass from the Glass Museum of Marinha Grande.

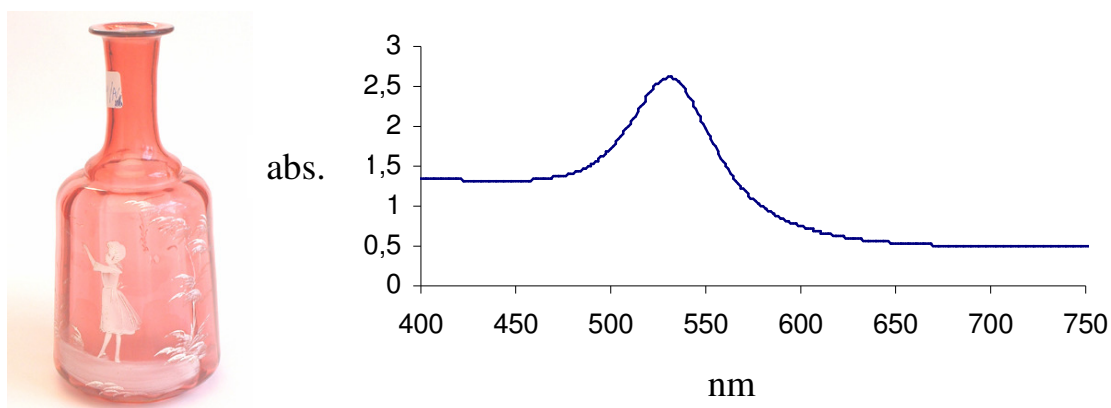
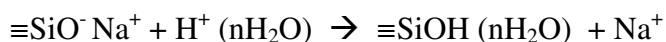


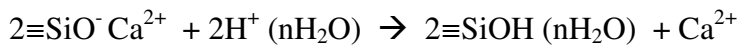
Fig. 6. Bottle of ruby gold glass, (prob.) Marinha Grande, 19th century and its optical absorption spectrum showing an absorption band with a maximum at about 530 nm.

In this case the gold could not be detected by XRF as the flask was made of lead crystal. Being lead a heavy element, it absorbed the characteristic X-ray emission of gold as its concentration in glass was certainly very low, probably around 0.01wt%. The absorption spectra unequivocally indicated the presence of gold.

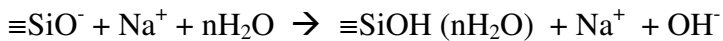
Chemical corrosion of glass

The chemical corrosion of glass is due to the contact of water (vapour or liquid) with the glass surface causing alkali/alkaline earth species exchange with H^+ (H_3O^+) [8] .



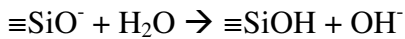
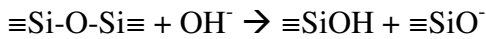


Another type of exchange is shown in the following reaction

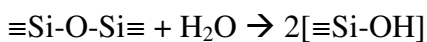


In any case, a layer of the surface of the glass is depleted of alkali.

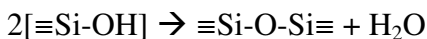
The presence of OH^- ions hydrolyses the $\equiv\text{Si-O-SiO}\equiv$ bonds.



The resulting reaction is



Condensation takes also place



and a silica gel layer is formed.

The contact of historical glasses with a humid environment causes the alteration phenomenon called crizzling which consists in fine cracks developed in glass as a consequence of poorly calculated batch, usually with an excess of alkali and insufficient stabilizer [9,10]. Archaeological glasses suffer chemical attack by natural agents and the weathering can be very destructive.

An example of the attack of glass objects by water is shown in Fig. 7.

Analytical techniques used for the characterization of glass - examples

Non destructive techniques that can be used for glass characterization are listed below:

Micro-EDXRF (energy dispersive micro X-ray fluorescence spectrometry)

UV-Vis-NIR (ultraviolet, visible and near infrared spectroscopy)

LIBS (laser induced breakdown spectroscopy)

ESEM (environmental scanning electron microscopy)

PIXE (proton induced X-ray emission) - with external ion beam

LA/ICP-MS (laser ablation inductively coupled plasma mass spectrometry)

Radiation measurement (for uranium and potassium analysis)

It is important to refer that the use of a laser leaves a very small mark not visible at naked eye.

As far as we know, there are two microdestructive sampling techniques used for glass analysis. One uses a diamond tip to take a very small amount of glass (a few micrograms) [11]. If the glass has some stress, there is the danger of breaking. The second method developed by Lopes et al [12] uses

a drop of diluted HF to dissolve the glass. The acid makes a very small mark so it should be applied only in a part of the artwork not visible when exhibited. In both methods the chemical analysis can be made either by ICP-MS or neutron activation analysis.



Fig.7. Attack of glass by water a) Crizzling, beginning - cloudy, hazy surface of glass; b) Crizzling, beginning - cloudy, wet, hydrated surface of glass ("sweating" or "weeping"); c) Crizzling, "full-blown", uniform cracking of the surface; d) Crizzling, advanced, surface beginning to flake, or exfoliate.

(courtesy of Stephen Koob of The Corning Museum of Glass, NY)

As destructive methods, which use small samples taken from glass fragments ICP-MS, PIXE, neutron activation analysis, scanning electron microscopy with energy dispersive X-ray emission spectrometry (SEM/EDX), atomic absorption spectroscopy, Electron Microprobe Analysis (EPMA), and laser ablation Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (LA/FTICRMS) can be used. Solid state nuclear magnetic resonance (NMR) can be a useful technique to study the silicon local structure.

A few examples will be given in order to illustrate the use of some of the techniques in the characterization of glass artefacts.

In recent work in our Laboratories, two glass production centres of the 18th century, Covina and Marina Grande, have been studied. The provenance of glasses from excavations, as well as from objects from national museum collections which seemed to be produced in Portugal, can only be unequivocally determined through analytical characterization. The archaeometric studies of glasses will have to deal first with the archaeological glasses taken from the sites where the glass manufactures have been made. Excavations were already made in the site where the manufacture of Coina was installed, and a large and important collection of glass samples were collected. The samples were analysed in our laboratories using micro-EDXRF. A typical spectrum made using micro-EDXRF is shown in Fig. 8.

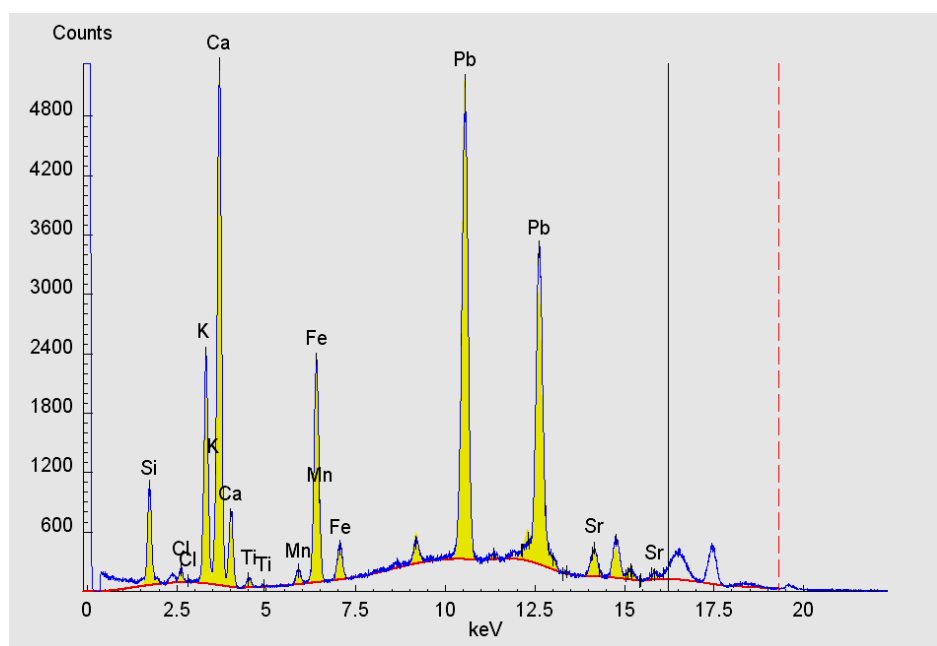


Fig. 8. micro-EDXRF spectrum using a portable spectrometer ArtTAX – glass fragment of lead glass of the “Real Fábrica de Vidros de Coina” indicating the elements Si, K, Ca, Mn, Fe, Sr and Pb.

A preliminary analysis of 29 fragments showed that they could be divided into the following four groups according to their chemical compositions: potash glass, soda-lime glass, high-lime low-alkali glass and lead glass (Fig. 9).

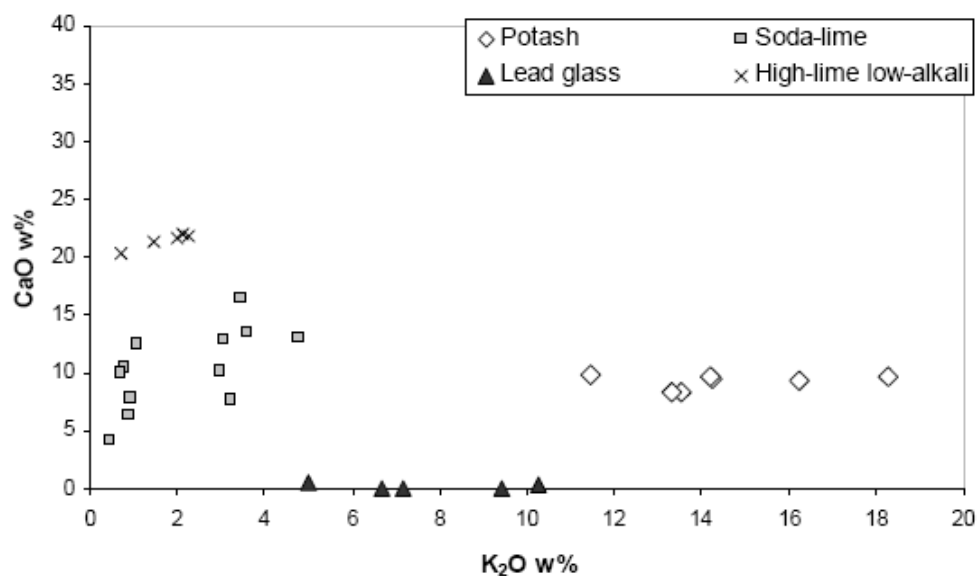


Fig. 9. Plot of potassium and calcium oxides contents for the Coina fragments [13].

One of the fragments showing weathering, characteristic of archaeological samples which have been in contact with water, was studied in detail. This fragment was from the archaeological Coina excavation (Fig. 10) [14].

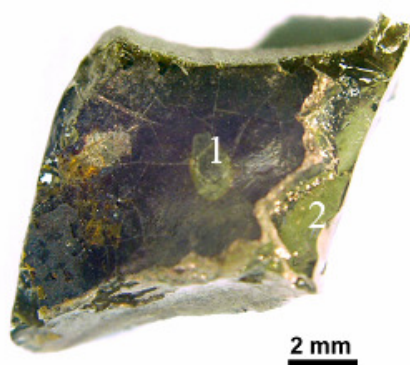


Fig. 10. Coina glass fragment: 1 - corroded surface; 2 - original green olive glass.

The use of SEM allowed the study of the different layers of corrosion as can be seen in the Figs. 11 and 12. The corrosion layer present fissures (or cracks) with two distinct phases, one heterogeneous and the other homogeneous. After identification of the elements present using SEM/EDX, the elements were chosen and a small area of the original fracture was scanned.

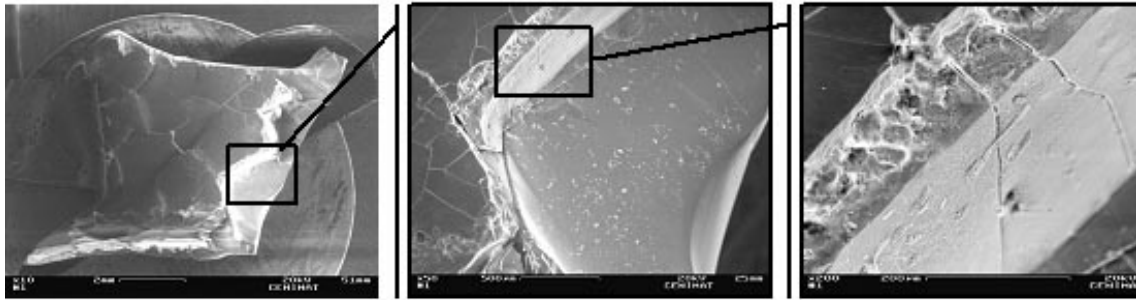
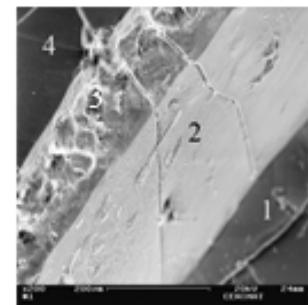
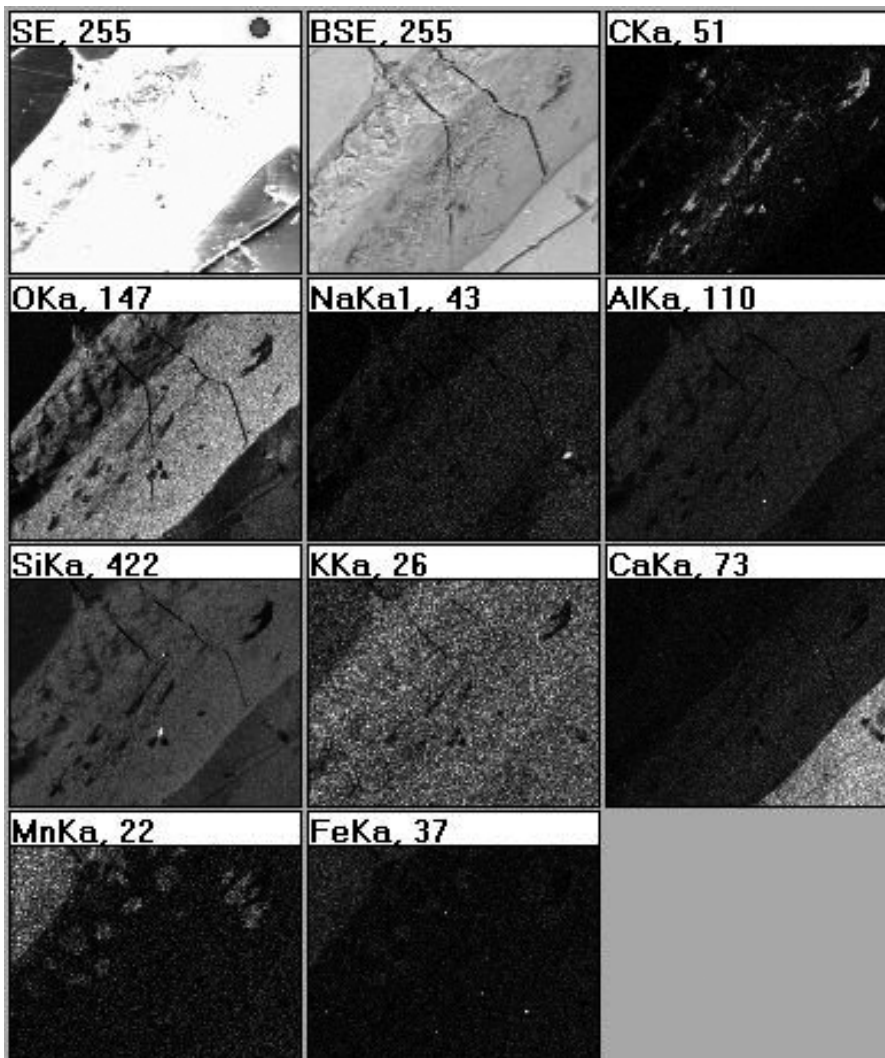


Fig. 11. SEM image of the glass fragment with increasing amplifications of a selected area; (a) area observed (x10); (b) area analysed (x50); (c) different layers showing the glass corrosion (x200).



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Original fracture
 1 - original glass of olive green colour;
 2 - corrosion crust yellow and translucent;
 3 - black inclusions in the crust;
 4 - blackened crust surface with cracks

Fig. 12. SEM/EDX of the corroded glass fragment.

Just a few comments are made here. There is an enrichment of silicon and aluminium at the surface as a consequence of the corrosion by water. Black conical inclusions observed at the surface have

an appreciable quantity of iron and manganese probably due to contamination from the soil. No calcium was lixiviated which may be due to a surface rich in silica and alumina.

Ion beam techniques are currently used for the analysis of glass surfaces. It is reported here the use of PIXE using a beam of protons of the Van de Graaff accelerator at the Portuguese Nuclear Institute to study the yellow silver staining [15]. Fig. 13 shows the characteristic spectrum of the yellow staining colour due to the presence of nanoparticles of silver.

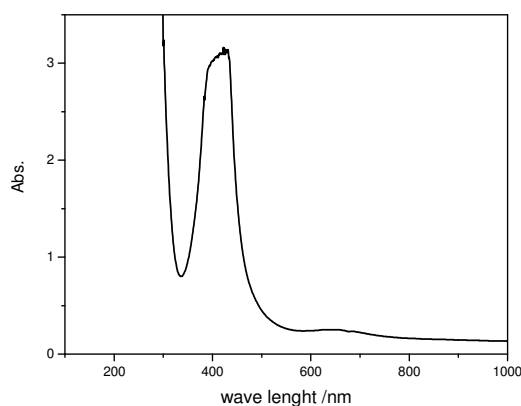


Fig. 13. UV-Vis spectrum of silver staining.

A typical example of the X-ray maps using PIXE obtained from a cross-section of a sample painted with yellow silver staining is shown in Fig. 14.

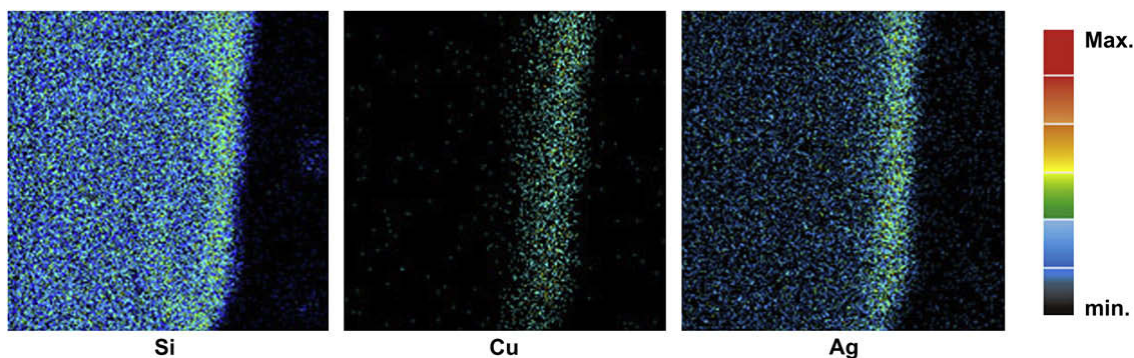


Fig. 14. Elemental X-ray maps of yellow silver staining ($106 \times 106 \mu\text{m}^2$) using PIXE.

It is possible to identify the simultaneous presence of Cu and Ag in the near surface region. However, while the former is clearly confined to this region, the latter distributes also in the glass bulk, indicating that diffusion of Ag into the glass matrix has occurred.

Another technique that has been explored in our Laboratories is Laser Ablation Fourier Transform Ion Cyclotron Resonance Mass Spectrometry which can be used to characterize glasses [16]. One interesting feature of this type of mass spectrometry is its high resolution, so isobars can be easily distinguished. The positive ion spectra give the main constituents of glass exception made to the

boron as no positive ions can be observed. At the same time the observation of several clusters in the negative ion spectra indicates the type of glass analysed. Figs. 15 and 16 show the mass spectra of two different types of glasses, a soda-lime silicate glass and a borosilicate glass. As can be seen the negative ion spectra are different for the two glasses. The negative ion spectrum of a soda-lime silicate glass gives a series of clusters with silicon, oxygen, sodium and aluminium. The spectrum of the borosilicate glass shows predominantly the ions BO_2^- , BONaH^- and BO_3H^- . Boron could not be seen in the positive ion spectrum.

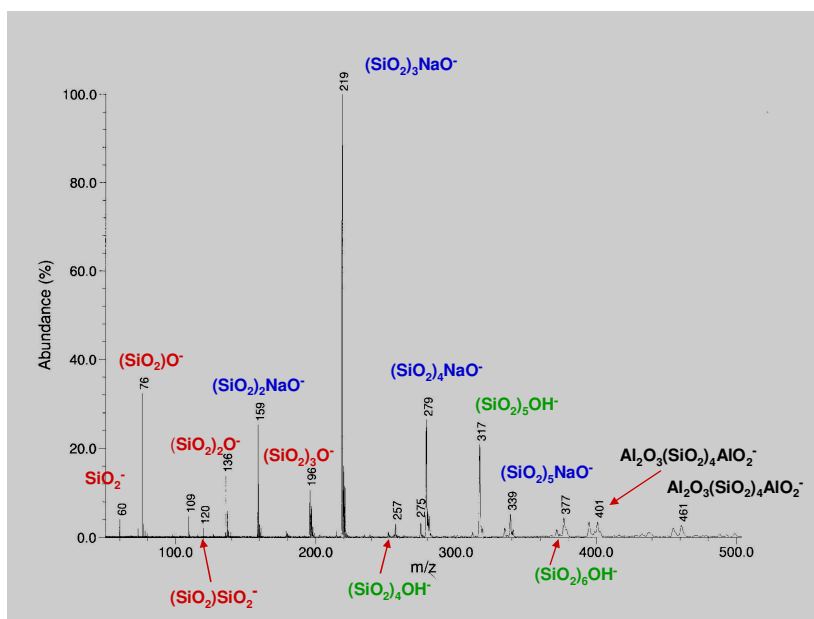


Fig. 15. Negative ion mass spectrum of a soda-lime silicate glass; the colours show the families of clusters observed.

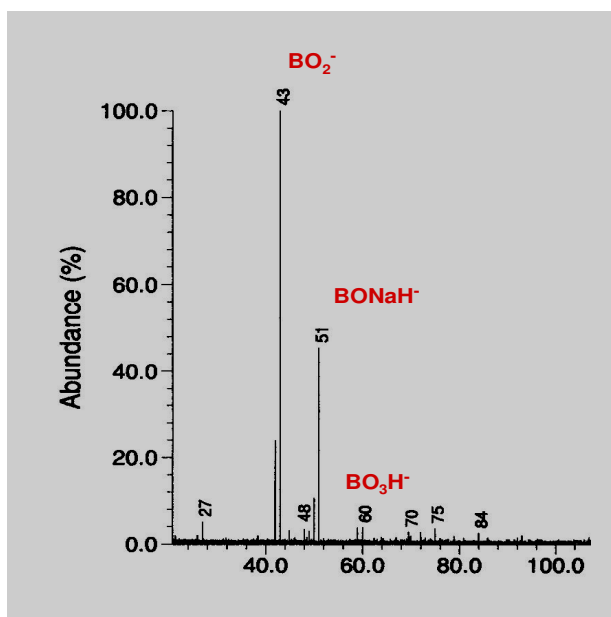


Fig. 16. Negative ion mass spectrum of a borosilicate glass

Final Remarks

In this short review it was shown that there are several techniques which can be used for glass characterization being their choice dependent essentially if destructive or non-destructive methods are to be used. A few examples were given either of simple chemical analysis of glass objects or of fragments having in mind provenance studies. In this short review no mention was made to the isotope ratio analysis, in particular oxygen and lead, which can contribute with important information in provenance studies. An example of the study of corrosion was given using SEM/EDXF, a technique widely employed also for the study of archaeological glass.

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